



Global Marine Products



Our Family of Brands

Everything You Need to Know About Marine Fuels





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This publication was prepared for Chevron Global Marine Products by Monique B. Vermeire of the Marine Lubricants and Fuels Technical Department, located at Chevron Technology Ghent in Belgium. Monique does exclusive work for Chevron Global Marine Products in the area of fuel technology, with related field support for matters concerning fuel quality issues. The Marine Lubricants and Fuels Technical Department actively supports Chevron Global Marine Products with international fuel projects and at industry seminars.



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I. Introduction



Liquid fuel...combustion...mechanical energy ...propulsion energy and electricity

Through thermal plants, marine engines and gas turbines, the energy obtained from fuel oil combustion is made available to fulfill our needs, be it for transport purposes or for electrical power applications.

From the early 19th century until the third quarter of the 20th century, steamships crossed the seven seas, gradually eliminating sailing ships from commercial shipping.

In the second half of the 20th century, the motor ship started to dominate. The history of the diesel engine began in 1892 with Rudolf Diesel and twenty years later, the first four-stroke marine diesel engine ships were operational.

Around 1930, two-stroke designs took a strong lead as ships became larger and faster.

Between World War I and World War II, the share of marine engine-driven ships increased to approximately 25 percent of the overall ocean-going fleet tonnage.

A series of innovations of the diesel engine followed, which made it possible to use heavy fuel oil in medium-speed trunk piston engines, pioneered by the MV *The Princess of Vancouver*. In the mid-1950s, high alkalinity cylinder lubricants became available to neutralize the acids generated by the combustion of high sulphur residual fuels, and wear rates became comparable to those found when using distillate diesel fuel.

Diesel ships using residual fuel oil gained in popularity and in the second half of the 1960s, motor ships overtook steamships, both in terms of numbers, and in gross tonnage. By the start of the 21st century, motor ships accounted for 98 percent of the world fleet.

Marine engines have also found their way into the power industry.





II. Crude Oil



1. How is a crude oil field formed?

The generally accepted theory is that crude oil was formed over millions of years from the remains of plants and animals that lived in the seas. As they died, they sank to the seabed, were buried with sand and mud, and became an organic-rich layer. Steadily, these layers piled up, tens of meters thick. The sand and mud became sedimentary rock, and the organic remains became droplets of oil and gas. Oil and gas passed through the porous rock and were eventually trapped by an impervious layer of rock, collecting at the highest point.

The formation of an oil/gas field requires the presence of four geological features:

- **Source rock:** contains suitable organic matter, which, under the conditions of heat and pressure, produces hydrocarbons
- **Reservoir rock:** a porous layer of rock in which the hydrocarbons are retained
- **Cap rock:** a rock or clay, which prevents the hydrocarbons from escaping
- **Trap:** a rock formation bent into a dome or broken by a fault which blocks the escape of the hydrocarbons either upward or sideways

Most importantly, these four factors have to occur at the right time, place and in the right order for oil and gas to be formed and trapped. Currently, successful petroleum exploration relies on modern techniques such as seismic surveying. The fundamental principle of seismic surveying is to initiate a seismic pulse at or near the earth's surface and to record the amplitudes and travel times of waves returning to the surface after being reflected or refracted from the interface(s) on one or more layers of rock. Once seismic data has been acquired, it must be processed into a format suitable for geological interpretation and petroleum reservoir detection.

2. Composition and classification of crude oil

Crude oil is a mixture of many different hydrocarbons and small amounts of impurities. The composition of crude oil can vary significantly depending on its source. Crude oils from the same geographical area can be very different due to different petroleum formation strata. Different classifications of crude oil are based on:

1. Hydrocarbons:

- Paraffinic crudes
- Naphtenic crudes
- Asphaltenic (aromatic) crudes

Each crude oil contains the three different types of hydrocarbons, but the relative percentage may vary widely. For example, there is paraffinic crude in Saudi Arabia, naphtenic crude in some Nigerian formations and asphaltenic crude in Venezuela.

2. American Petroleum Institute (API) gravity: The lower the density of the crude oil, the higher its API gravity. A higher API gravity means that the crude contains more valuable lower boiling fractions.

3. Sulphur content: The ever-growing concern for the environment and the impact on refining cost calculations are the basis for this classification.

- Low sulphur crude
- High sulphur crude

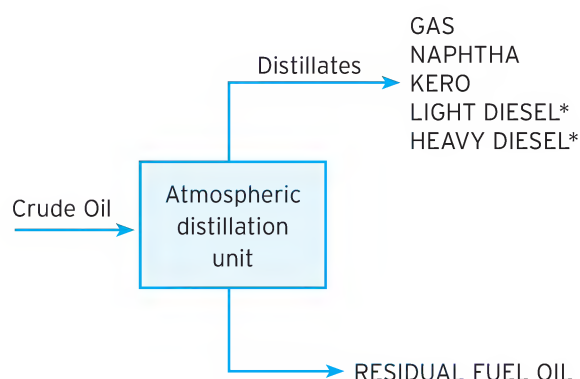
3. Crude oil refining and stocks for marine fuel blending

Petroleum refineries are a complex system of multiple operations. The processes used at a given refinery depend upon the desired product slate and characteristics of the crude oil mix. Today, complex refining has a definite impact on the characteristics of marine diesel and intermediate fuel oil (IFO) bunker fuel.

Typical refining schemes and the influence on marine fuels

Straight run refinery

Atmospheric crude distillation and further refining of distillates:



* Diesel refers here to specific atmospheric distillation cuts, and is not related to an engine application.

the cutterstocks used. The high amount of paraffinic hydrocarbons in the straight run marine fuels leads to relatively low densities for these products, ensuring easy and efficient onboard fuel purification.

The product slate of a straight run refinery, with its heavy fuel production of approximately 50% of the crude feed, does not correspond to the product demand in industrialized countries where the ever-growing demand for light products (jet fuel, gasoline, and gasoil) coincides with a strong reduction in the demand for heavy fuel (10 to 15% of the crude oil). This results in the need to convert the residue fraction into lighter, hence, more valuable, fractions and to the construction of complex refineries.

A complex refinery processing scheme can be separated into two parts:

1. Crude oil distillation (atmospheric and vacuum distillation)
2. Streams from the vacuum distillation unit are converted through catalytic and thermal cracking processes.

Straight run stocks for marine fuel blending

Light diesel, heavy diesel, and straight run residue

Straight run marine gasoil and distillate marine diesel (MDO)

Marine gasoil and distillate marine diesel oil (MDO) are manufactured from kero, light, and heavy gasoil fractions. For DMC distillate marine diesel up to 10-15%, residual fuel can be added.

Straight run IFO 380 mm²/s (at 50°C)

This grade is obtained by blending the atmospheric residue fraction (typical viscosity of about 800 mm²/s at 50°C) with a gasoil fraction.

Straight run lower viscosity grade IFOs

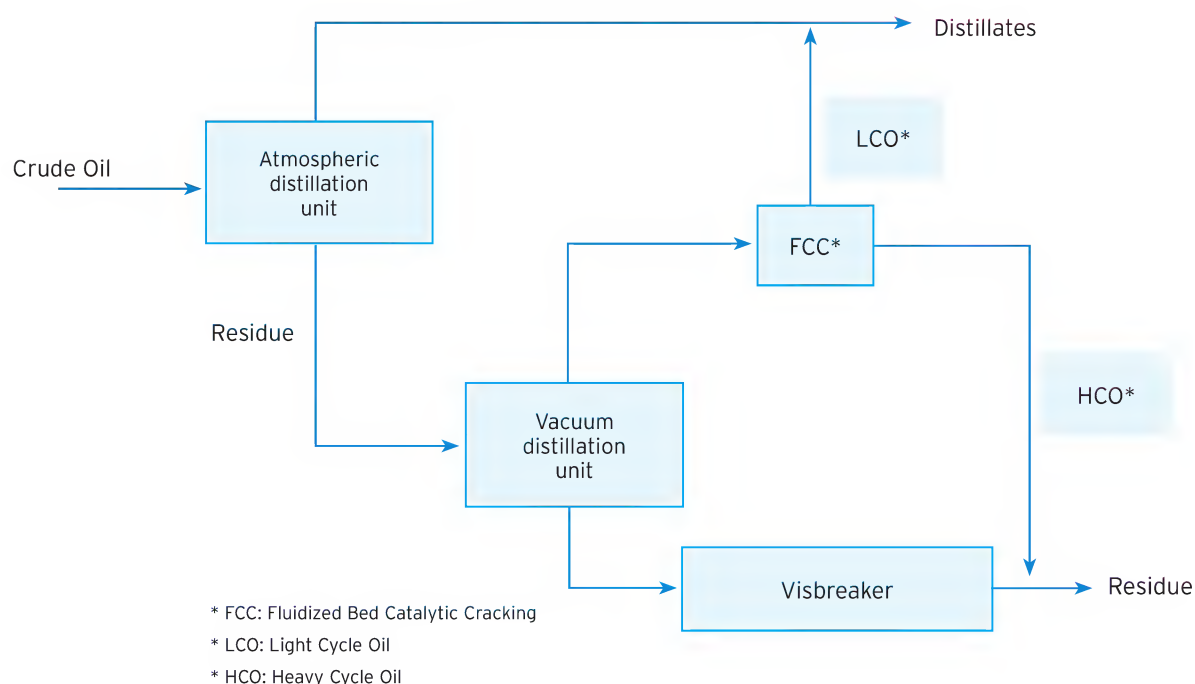
Blending to lower grade IFOs is done from the IFO 380 mm²/s (at 50°C) using a gasoil cutter stock or with marine diesel.

All IFOs have good ignition characteristics, due to the high percentage of paraffinic material still present in the atmospheric residue, and the paraffinic nature of





Example: Complex refinery with (fluid) catalytic cracking and visbreaking



Complex refineries have been favored since the early 1980s and are intended to boost gasoline production. All further information herein is based on a complex refinery. The main marine fuel blending components from a fluidized bed catalytic cracking (FCC) refinery with visbreaker are the same distillates as those from a straight run refinery (light and heavy diesel) as well as light cycle (gas) oil (LC(G)O) and heavy cycle oil (HCO) from the catcracker and visbroken residue from the visbreaker.

Atmospheric residue is used as feedstock for the vacuum unit and will seldom be available for fuel blending.

More detailed information on complex refining is provided in Attachment I.

Marine fuels resulting from a catalytic cracking/visbreaking refinery have a composition that is markedly different from that of an atmospheric refinery.

Marine gasoil (MGO/DMA)

A new blend component has appeared – light cycle (gas) oil – that contains about 60% aromatics. Due to the high aromatic nature of LC(G)O, the density of a marine gasoil blended with LC(G)O will be higher than when using gasoil from an atmospheric distillation refinery. The density will typically be close to 860 kg/m³ (at 15°C). No performance or handling differences with atmospheric gasoil are to be expected.

Note: Marine gasoil S max. legislation usually follows that of gasoil for inland use. This is the case in the European Union (EU) where the max. S level of marine gasoil for use in territorial waters is currently 0.20 m/m % max. and subject to decrease to 0.10 m/m % max in 2008. This has an effect on the acidity of the combustion gases, and the alkalinity (BN) and dispersancy of the lubricant may have to be adjusted accordingly.



Due to logistics, it is possible that in some areas marine gasoil is, in fact, automotive diesel (with added marker and dye and without the excise duty applicable to automotive fuel). Currently in the EU a max. S level is 0.0050 m/m % max., and subject to decrease to 0.0010 m/m % max. in 2009. Again, the alkalinity (BN) and dispersancy of the lubricant may have to be adjusted accordingly.

Distillate marine diesel (MDO/DMB)

Distillate marine diesel (commercial denomination) typically has a lower cetane index than marine gasoil, and has a higher density. With the production slate of a catalytic cracking refinery, distillate marine diesel can therefore contain a higher percentage of LC(G)O than marine gasoil.

Note: Worldwide, marine diesel has a sulphur content between approx. 0.3 and 2.0 m/m %. Due to recent EU legislation (Directive 2005/33/EC amending Directive 1999/32/EC), the sale of marine diesel oil with a sulphur content above 1.5 m/m % within the EU is prohibited as of August 11, 2006.

Blended marine diesel (MDO/DMC)

With atmospheric refining, blended marine diesel (MDO/DMC) can contain up to 10% IFO with either marine gasoil (MGO/DMA) or distillate marine diesel (MD)/DMB). With complex refining, MDO/DMC no longer corresponds to a specific composition and extreme care must be used when blending this grade to prevent stability and/or combustion problems.

IFO-380

This grade is usually manufactured at the refinery and contains visbroken residue, HCO and LC(G)O. These three components influence the characteristics of the visbroken IFO-380.

Vacuum distillation reduces the residue yield to about 20% of the crude feed, unavoidably leading to a concentration of the heaviest molecules in this fraction. Visbreaking converts about 25% of its vacuum residue feed into distillate fractions. This means that about 15% of the original crude remains as visbroken residue. The asphaltenes¹, sulphur and metal content in visbroken residue are 3 to 3.5 times higher than in atmospheric

residue. Visbreaking affects the molecular structure: Molecules are broken thermally, and this can deteriorate the stability of the asphaltenes.

HCO (typical viscosity at 50°C: 130 mm²/s) contains approximately 60% aromatics, and is a high-density fraction: the density at 15°C is above 1 kg/l (typically 1.02). It is the bottom fraction of the FCC unit. The catalytic process of this unit is based on an aluminum silicate. Some mechanical deterioration of the catalyst occurs in the FCC process, and the resulting cat fines are removed from the HCO in the refinery. This removal, however, is not 100% efficient and a certain amount (ppm level) of cat fines remains in the HCO. From there they end up in heavy fuel blended with HCO. (See also Chapters III-2)

The aromaticity of HCO assists in ensuring optimum stability for the visbroken fuel blend.

LC(G)O (typical viscosity at 50°C: 2.5 mm²/s) has the same aromaticity as HCO, but is a distillate fraction of the FCC unit, with a distillation range comparable to that of gasoil. With a typical density of 0.94 kg/l at 15°C, it is used to fine-tune the marine heavy fuel oil blending where generally a density maximum limit of 0.9910 kg/l has to be observed.

IFOs < 380 mm²/s

These grades are generally blended starting from 380 mm²/s IFOs (at 50°C), by using a suitable cutterstock (marine diesel, gasoil, LC(G)O, or a mixture of these). The blend composition has to be construed in such a way that the product stability is safeguarded, while at the same time direct or indirect density limits are fulfilled. (See also Chapters III-2)



¹ Asphaltenes: residual fuel components that are insoluble in heptane but soluble in toluene

III. Fuel Oil

1. Fuel oil applications

All fuel oil applications create energy by burning fuel oil. Fuel oil combustion (oxidation reaction) releases a large amount of heat, which can be used for steam generation, for example, in steam turbines. The high volume (pressure) of the combustion gases can be used to drive an engine, or (less frequent for HFO, but widespread for gasoil) a gas turbine.

When fuel oil is burned, an amount of heat is released, which is defined by the specific energy (international unit MJ/kg) of the fuel.

Thermal plants use this heat to generate steam, which then drives steam turbines, thus providing mechanical energy that can be used for propulsion or to be converted into electrical energy.

For marine engines and gas turbines, mechanical energy provided by the combustion gases is used either directly for propulsion or converted into electrical energy for power plants. For larger installations, cost efficiency optimization and environmental constraints led to the introduction of co-generation. In co-generation, some of the electrical energy lost is used to generate low-pressure steam, suitable for a wide range of heating applications.

2. Fuel specifications

Different types of fuel oil applications and environmental considerations have led to different types of fuel oil specifications. These are much more demanding than the original fuel oil n° 6 or Bunker C requirements when all heavy fuel was used for thermal plants and steam turbines. Emission standards for thermal plants can vary widely, depending on the geographical area. Since all emitted SO₂ originates from sulphur in the fuel, emission standards on SO₂ automatically limit the sulphur content of the fuel, except for large combustion plants, where the standard can be economically met by flue gas desulphurization.

In the late 1960s, marine diesel engines were the primary means of ship propulsion. Through the late 1970s, marine engine heavy fuel oil grades remained identified solely by their maximum viscosity. This worked well with heavy fuel originating from atmospheric refineries. Fuel-related operational problems arose with the generalized upgrading of refinery operations

in the second half of the 1970s from straight run to complex refining.

1982 saw the publication of marine fuel specification requirements by the British Standard Organization (BS MA 100), and by CIMAC (Conseil International de Machines à Combustion).

An international ISO standard has existed since 1987: ISO 8217. The stated purpose of ISO 8217 is to define the requirements for petroleum fuels for use in marine diesel engines and boilers, for the guidance of interested parties such as marine equipment designers, suppliers and purchasers of marine fuels. These specifications are regularly revised to accommodate changes in marine diesel engine technology, crude oil refining processes and environmental developments. The ISO 8217:2005 specifications for marine fuels will be discussed in detail in Chapter III-2a (see pages 8 & 9, Tables 1 & 2).

The most important specifications to ensure reliable engine operation with fuel originating from complex refining are:

- Maximum density limit: Important for classical purifier operation and to ensure satisfactory ignition quality for low viscosity fuel grades
- Maximum Al+Si limit: In a complex refinery, HCO is used as a blending component. Mechanically damaged aluminum silicate catalyst particles of the catalytic cracker are not completely removed from the HCO stream, and are found back in mg/kg amounts in heavy fuel blended with HCO. In order to avoid abrasive damage in the fuel system onboard the vessel, it is necessary to limit the amount of Al+Si to a level, which can be adequately removed by the ship's fuel cleaning system.
- Maximum total potential sediment limit: The stability of asphaltenes is deteriorated by the visbreaking process, and instability problems can cause fuel purification and filter-blocking problems, hence the need for a specification to ensure adequate fuel stability.

A less widespread application of heavy fuel is found in heavy-duty gas turbines: Here the fuel specification requirements before the injection are very severe, and can only be obtained by an extremely thorough precleaning of the fuel.

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Table 1: Requirements for marine distillate fuels

Characteristic	Unit	Limit	Category ISO-F				Test method reference
			DMX	DMA	DMB	DMC ^a	
Density at 15°C	kg/m ³	max.	–	890.0	900.0	920.0	ISO 3675 or ISO 12185 (see also 7.1)
Viscosity at 40°C	mm ² /s ^b	min. max.	1.40 5.50	1.50 6.00	– 11.0	– 14.0	ISO 3104 ISO 3104
Flash point	°C	min. min.	– 43	60 –	60 –	60 –	ISO 2719 (see also 7.2)
Pour point (upper) ^c - winter quality - summer quality	°C	max. max.	– –	–6 0	0 6	0 6	ISO 3016 ISO 3016
Cloud point	°C	max.	–16	–	–	–	ISO 3015
Sulfur ^c	% (m/m)	max.	1.00	1.50	2.00 ^e	2.00 ^e	ISO 8754 or ISO 14596 (see also 7.3)
Cetane index	–	min.	45	40	35	–	ISO 4264
Carbon residue on 10% (V/V) distillation bottoms	% (m/m)	max.	0.30	0.30	–	–	ISO 10370
Carbon residue	% (m/m)	max.	–	–	0.30	2.50	ISO 10370
Ash % (m/m)	% (m/m)	max.	0.01	0.01	0.01	0.05	ISO 6245
Appearance ^f	–	–	Clear and bright		f	–	See 7.4 and 7.5
Total sediment, existent	% (m/m)	max.	–	–	0.10 ^f	0.10	ISO 10307-1 (see 7.5)
Water	% (V/V)	max.	–	–	0.3 ^f	0.3	ISO 3733
Vanadium	mg/kg	max.	–	–	–	100	ISO 14597 or IP 501 or IP 470 (see 7.8)
Aluminium plus silicon	mg/kg	max.	–	–	–	25	ISO 10478 or IP 501 or IP 470 (see 7.9)
Used lubricating oil (ULO) - Zinc - Phosphorus - Calcium	mg/kg mg/kg mg/kg	max. max. max.	– – –	– – –	– – –	The fuel shall be free of ULO ^g 15 15 30	IP 501 or IP 470 IP 501 or IP 500 IP 501 or IP 470 (see 7.7)

a Note that although predominantly consisting of distillate fuel, the residual oil proportion can be significant.

b 1 mm²/s = 1 cSt

c Purchasers should ensure that this pour point is suitable for the equipment on board, especially if the vessel operates in both the northern and southern hemispheres.

d This fuel is suitable for use without heating at ambient temperatures down to –16°C.

e A sulfur limit of 1.5 % (m/m) will apply in SOx emission control areas designated by the International Maritime Organization, when its relevant protocol enters into force. There may be local variations, for example the EU requires that sulphur content of certain distillate grades be limited to 0.2 % (m/m) in certain applications.

f If the sample is clear and with no visible sediment or water, the total sediment existent and water tests shall not be required.

g A fuel shall be considered to be free of used lubricating oils (ULOs) if one or more of the elements zinc, phosphorus and calcium are below or at the specified limits. All three elements shall exceed the same limits before a fuel shall be deemed to contain ULOs.

Table 2: Requirements for marine residual fuels

Characteristic	Unit	Limit	Category ISO-F										Test method reference
			RMA 30	RMB 30	RMD 80	RME 180	RMF 180	RMG 380	RMH 380	RMK 380	RMH 700	RMK 700	
Density at 15°C	kg/m ³	max.	960.0	975.0	980.0	991.0		991.0		1010.0	991.0	1010.0	ISO 3675 or ISO 12185 (see also 7.1)
Kinematic viscosity at 50°C	mm ² /s ^a	max.	30.0		80.0	180.0		380.0		700.0		ISO 3104	
Flash point	°C	min.	60		60	60		60		60		ISO 2719 (see also 7.2)	
Pour point (upper) ^b	°C	max.	0	24	30	30		30		30		ISO 3016	
- winter quality	°C	max.	6	24	30	30		30		30		ISO 3016	
- summer quality	°C	max.	6	24	30	30		30		30		ISO 3016	
Carbon residue	% (m/m)	max.	10		14	15	20	18	22		22		ISO 10370
Ash	% (m/m)	max.	0.10		0.10	0.10	0.15	0.15		0.15		ISO 6245	
Water	% (V/V)	max.	0.5		0.5	0.5		0.5		0.5		ISO 3733	
Sulfur ^c	% (m/m)	max.	3.50		4.00	4.50		4.50		4.50		ISO 8754 or ISO 14596 (see also 7.3)	
Vanadium	mg/kg	max.	150		350	200	500	300	600		600		ISO 14597 or IP 501 or IP 470 (see 7.8)
Total sediment potential	% (m/m)	max.	0.10		0.10	0.10		0.10		0.10		ISO 10307-2 (see 7.6)	
Aluminium plus silicon	mg/kg	max.	80		80	80		80		80		ISO 10478 or IP 501 or IP 470 (see 7.9)	
Used lubricating oil (ULO)	mg/kg	max. max. max.	The fuel shall be free of ULO ^d										IP 501 or IP 470 (see 7.7) IP 501 or IP 500 (see 7.7) IP 501 or IP 470 (see 7.7)
- Zinc													
- Phosphorus													
- Calcium													

a Annex C gives a brief viscosity/temperature table, for information purposes only. 1 mm²/s = 1 cSt

b Purchasers should ensure that this pour point is suitable for the equipment on board, especially if the vessel operates in both the northern and southern hemispheres.

c A sulfur limit of 1.5 % (m/m) will apply in SOx emission control areas designated by the International Maritime Organization, when its relevant protocol comes into force. There may be local variations.

d A fuel shall be considered to be free of ULO if one or more of the elements zinc, phosphorus and calcium are below or at the specified limits. All three elements shall exceed the same limits before a fuel shall be deemed to contain ULO.



The fuel treatment consists of the removal of the alkali metals by fuel precleaning and inhibition of vanadium-induced corrosion by injecting magnesium-containing additives that react with the vanadium to form non-corrosive compounds. The heavy-duty gas-turbine application of heavy fuel is further discussed in Attachment II.

2a. Significance of the marine fuel properties listed in ISO 8217:2005

Kinematic viscosity:

Kinematic viscosity is a measure for the fluidity of the product at a certain temperature. The viscosity of a fuel decreases with increasing temperature. The viscosity at the moment the fuel leaves the injectors must be within the limits prescribed by the engine manufacturer to obtain an optimal spray pattern. Viscosity outside manufacturers' specifications at the injectors will lead to poor combustion, deposit formation and energy loss. The viscosity of the fuel must be such that the required injection viscosity can be reached by the ship's preheating system.

Density:

The official unit is kg/m³ at 15°C, while kg/l at 15°C is the most commonly used unit. Density is used to calculate the quantity of fuel delivered. The density gives an indication of the ignition quality of the fuel within a certain product class. This is particularly the case for the low-viscosity IFOs. The product density is important for the onboard purification of the fuel; the higher the density, the more critical it becomes (see Chapter III-4 on fuel oil treatment).

Cetane index:

Cetane index is only applicable for gasoil and distillate fuels. It is a measure for the ignition quality of the fuel in a diesel engine. The higher the rpm of the engine, the higher the required cetane index. The cetane index is an approximate calculated value of the cetane number, based on the density and the distillation of the fuel. The cetane index is not applicable when cetane-improving additives have been used.

Carbon residue:

Carbon residue is determined by a laboratory test performed under specified reduced air supply. It does

not represent combustion conditions in an engine.

It gives an indication of the amount of hydrocarbons in the fuel which have difficult combustion characteristics, but there is no conclusive correlation between carbon residue figures and actual field experience. The micro carbon residue method is specified by ISO 8217.

Ash:

The ash content is a measure of the metals present in the fuel, either as inherent to the fuel or as contamination.

Flash point:

Flash point is the temperature at which the vapors of a fuel ignite (under specified test conditions), when a test flame is applied. The flash point for all fuels to be used in bulk onboard vessels is set at PM, CC, 60°C minimum (SOLAS agreement). DMX, a special low cloud point gasoil, may only be stored onboard in drums because of its < 60°C flash point.

Sulphur:

The sulphur content of a marine fuel depends on the crude oil origin and the refining process. When a fuel burns, sulphur is converted into sulphur oxides. These oxides reach the lubricating oil via the blow-by gas. These oxides are corrosive to engine piston liners and must be neutralized by the cylinder lubricant. Marine engine lubricants are developed to cope with this acidity (high BN). If the correct lubricant is used, the sulphur content of a marine fuel is technically not important but may have environmental implications.

Therefore, Annex VI to Marpol 73/78 currently requires the sulphur content of any fuel oil used onboard ships not to exceed 4.5 m/m % max. In 2006, both Annex VI and the EU directive 2005/33/EC have restricted the SO_x emissions of ships sailing in the Baltic Sea SECA (Sulphur oxides Emission Control Area) to 6 g/kWh which corresponds to a fuel oil sulphur content of maximum 1.5 m/m %. In addition, the EU directive extended the 1.5 m/m % S limit to ferries operating to and from any EU port. In 2007, the North Sea and English channel will become a SECA area where the 1.5 m/m % S limit will also apply.

The EU directive also has set a limit of 0.1 m/m% max on the sulphur content of marine fuels used by ships at berth (and by inland waterways), effective January 1, 2010.

The process to review already enacted environmental legislation in order to further reduce emissions has already started. Therefore, the limits and requirements stated above are subject to change.

Water content:

Water in fuel is a contamination and does not yield any energy. The percentage of water in the fuel can be translated into a corresponding energy loss for the customer. Water is removed onboard the vessel by centrifugal purification. If after purification, the water content remains too high, water vapor lock can occur and pumps can cut out. If water-contaminated fuel reaches the injectors, combustion can be erratic. Water in fuel that remains standing in lines for a longer period can cause corrosion.

Pour point:

Pour point is the lowest temperature at which a fuel will continue to flow when it is cooled under specified standard conditions. Contrary to straight run heavy fuels (pour point typically in the +w20°C range), bunker fuels from a complex refinery generally have pour points below 0°C (range -10 to -20°C). This is because bunker fuel tanks are usually not completely heated – only before the fuel transfer pump. This can then lead to problems if a vessel receives high pour straight run bunker fuel. For distillate marine diesel, the cold temperature behavior is controlled in ISO 8217 by a pour point maximum. With marine diesels with a high content of heavier n-paraffins, vigilance is required if strong temperature changes are expected. (Wax settling can occur, even when the pour point specification is met.)

Elements:

Vanadium and nickel are elements found in certain heavy fuel oil molecules (asphaltenes). Upon combustion, vanadiumoxides are formed, and some have critical melting temperatures. The most critical are the double oxides/sulphates with sodium. Some countries have implemented maximum Ni concentrations for inland use of heavy fuel.

Total sediment potential:

Inorganic material naturally occurring in crude oil is removed in the refineries prior to the atmospheric distillation. Some minor contamination (for example, ironoxides) of a finished heavy fuel can not be excluded.

The biggest risk for sediment formation in heavy fuel is due to potential coagulation of organic material inherent to the fuel itself. Visbroken asphaltenes, if insufficiently stable, can form sediment (coagulation is influenced by time and temperature). A decrease in aromaticity of the fuel matrix by blending with paraffinic cutterstocks can also deteriorate the stability of the asphaltenes. In cases of heavy fuel instability, only a relative small fraction of the asphaltenes forms sediment, but this organic sediment includes in its mass some of the fuel itself, and water (onboard purifying problems), and the amount of generated sludge can become quite high. The total potential sediment is the total amount of sediment that can be formed under normal storage conditions, excluding external influences. If the total potential sediment of the heavy fuel oil markedly exceeds the specification value (0.10% m/m max) for all grades of IFOs and HFOs), problems with the fuel cleaning system can occur, fuel filters can get plugged and combustion can become erratic.

Catalytic fines:

Heavy cycle oil is used worldwide in complex refining as a blending component for heavy fuel. Mechanically damaged catalyst particles (aluminum silicate) cannot be removed completely in a cost-effective way, and are found in blended heavy fuel. Fuel precleaning onboard ships has a removal efficiency of approximately 80% for catalytic fines. In order to avoid abrasive wear of fuel pumps, injectors and cylinder liners the maximum limit for Al+Si defined in ISO 8217 is 80 mg/kg.

Used lubricating oil (ULO):

The use of used lubricants (predominantly used motor vehicle crankcase oils) in marine fuels first surfaced as a potential problem in the mid-1980s. Both CIMAC and ISO 8217 working groups have discussed the technical and commercial considerations at length. Calcium, zinc and phosphorous are considered “fingerprint” elements of ULOs, and limits for these elements have been set in ISO 8217:2005. A fuel oil is considered to contain ULO only when all three elements simultaneously exceed these limits. This, however, does not necessarily imply that the fuel oil is not suitable for use. Generally, 10 mg/kg Zn corresponds to approximately 1% used oil in the fuel. This is only an approximation; the zincdithiophosphate content of lubricants can vary considerably.

Calculated carbon aromaticity index (CCAI):

CCAI is an indicator of the ignition delay of an IFO. CCAI is calculated from the density and the viscosity of the fuel oil. Although it is not an official specification, it has found its way into many users' bunker fuel specification requirements. Some manufacturers specify CCAI limits for their engines, depending on engine type and application.

2b. Correspondence of specifications and test methods

ISO 8217:2005 lists test requirements and methods for testing. While these methods should be used worldwide for testing marine fuels, experience has shown that they are not. In some areas, precursors of the presently defined ISO methods are still being used. The correspondence (discrepancy) between such test methods/results and the test methods/data of ISO 8217 are described hereafter.

Density:

The mass (weight in vacuum) of the liquid per unit volume at 15°C. Official unit: kg/m³. Often used variant: kg/l. The density limits in ISO 8217 are expressed in kg/m³. Specific gravity 60/60°F: Specific gravity is the ratio of the mass of a given volume of liquid at 60°F to the mass of an equal volume of pure water at the same temperature. No unit.

API gravity:

A function of the specific gravity 60/60°F. API gravity is expressed as degrees API.

API gravity, deg = $(141.5 / \text{spec. gr. } 60/60^\circ\text{F}) - 131.5$

Micro Carbon Residue (MCR):

MCR is the carbon residue test prescribed by ISO 8217:2005. Formerly, the carbon residue test was Conradson Carbon Residue. MCR is quicker and more precise than CCR.

Al+Si:

The ISO 8217 prescribed test methods are ISO 10478 or IP 501 or IP 470. Only these methods and fully equivalent methods from national standardization organizations should be used. A former industry-wide limit for catalyst fines in heavy fuel was defined on Al alone (30 mg/kg max.). The ratio between Al and Si can,

however, vary considerably between different types and manufacturers of aluminum silicate catalyst. This is why the test measures the sum of Al and Si. In practice, the two ways of limiting the catalytic fines content in heavy fuel give the same degree of protection.

Total sediment existent and total sediment potential:

Differentiation can be made between tests for inorganic sediment and organic sediment, existent sediment and potential sediment.

According to ISO 8217:2005, the former limit on inorganic sediment (rust, sand) applicable to DMB marine diesel has been replaced by the requirement to measure the total sediment existent (ISO 10307-1) on all DMB category products that fail the visual inspection requirement to be free from visible sediment and water.

Organic type sediment can occur in DMB and DMC marine diesel and in intermediate fuel oils. The cause of the formation of organic sediment resides in the thermal cracking of the heaviest molecules of crude, generally in visbreaking operations. Asphaltenes, the heaviest molecules of crude, can become unstable by thermal cracking, and must be carefully monitored by the refineries. Once visbroken, the asphaltenes are more or less sensitive to changes in the aromaticity of the total fuel matrix. This must be taken into account for fuel blending when using visbroken heavy fuel and gasoil (paraffinic) blending stocks. The asphaltene sediment formation is a function of time and temperature (excluding external influences), and an unstable fuel will only reach its final sediment formation after a certain storage time. The sediment present in a sample of heavy fuel at a certain moment is given by the total existent sediment test, but there is no certainty that this figure corresponds to the condition of the bulk of the fuel at that same time. The total potential sediment test shows the total amount of sediment that can be formed under normal storage conditions, excluding external influences. The prescribed test method is ISO 10307-2 (IP 390+375 is equivalent).

The test method originally used in the industry for determining the total sediment was the Shell Hot Filtration Test. The test results can be existing sediment or potential sediment, depending on the ageing procedure. The results of this test are not equivalent to those of ISO 10307-2, due to a difference in the solvent used for the test. The Shell Hot Filtration Test with ageing generally gives slightly higher results.



Viscosity:

Kinematic viscosity is the only accepted method, expressed in mm²/s at a certain temperature. ISO 8217:2005 lists the maximum kinematic viscosities at 50°C (note: 1 mm²/s = 1cSt). SSU, SSF and RW1 (Saybolt Seconds Universal, Saybolt Seconds Furol and Redwood No. 1) are obsolete units.

3. Test specifications and precision

ISO 8217:2005 not only specifies the requirements for marine distillate and residual fuels and the test method references, it also lists ISO 4259:1992, "Petroleum products – determination and application of precision data in relation to methods of test".

The application of precision data in relation to methods of test automatically assumes that acquiring the sample was performed to the best industry standard possible, and that the sample is representative for the supply. Experience shows that the sample itself is often the weakest point in the chain. Chevron recognizes only the bunker fuel retain samples taken by its representative (for example, bunker barge attendant) at the moment of bunkering as valid.

Should a dispute arise due to a difference between test data obtained on valid retain samples by two different laboratories (one acting on behalf of the supplier, the other on behalf of the customer), ISO 4259 should be used to evaluate the validity of the results. If the reproducibility of the test method is met, both values are considered acceptable, and the average of the two is taken as the true value. If the reproducibility is not met, both results have to be rejected, and the guidelines set forth in ISO 4259 should be followed to solve the problem. This can be very time-consuming, and is very seldom done in practice. Both parties generally agree to the use of a third laboratory, the result of which will then be binding for both parties.

Let it be noted that reproducibility limits are only applicable between two analysis figures on the same sample (or samples considered as being the same). The reproducibility of a test method may not be invoked to explain a deviation against a specification limit.

The testing margin, however, has an effect on a single result; for example, the analysis result on a certain specification test obtained by the end user. If the end user has no other information on the true value of the characteristic than a (single) test result, the product fails

when the result exceeds the specification limit by more than 0.59R upper limit (where R is reproducibility of the test method), and more than 0.59R lower limit.

The significance of reproducibility should not be underestimated. It is the basis for all quality control against specifications. Without reproducibility data, test results would lose a major part of their significance, since there would be no way to define how close a test result approaches the true value.

Attachment II lists the methods for marine fuel testing listed in ISO 8217:2005, together with reproducibility. Whenever national standardization methods of testing are used, the full correspondence with the ISO prescribed method has to be checked. There can also be some differences in the precision data.

4. Onboard fuel oil treatment

In the late 1970s, the increasing market demand for distillate fuels (gasoline, diesel) and the resulting changes in refinery processes to cope with this demand, resulted in a deterioration of heavy fuel quality. Efficient cleaning of heavy fuel oil is mandatory to achieve reliable and economical operation of diesel engines burning heavy fuel.

Examples:

- Water is a common contaminant in fuel oil. Except for water content in the fuel oil due to transport, there can be a further contamination in the storage tank due to water condensation as a result of temperature changes.
- Catalyst fines from aluminum silicate catalyst used in the catalytic cracking process may end up in the heavy fuel and need to be removed to avoid abrasive wear of various engine parts.

Fuel from the storage tank is pumped to the settling tank and contaminants (water, solids) sink to the bottom of the tank under influence of the gravity force (g). The rate of separation by gravity, V_g is defined by Stokes' law:

$$V_g = [d^2 (D_2 - D_1) / 18 \eta] g$$

d: particle diameter

D_2 : particle density

D_1 : density of the fuel oil

η : viscosity of the fuel oil

g: gravitational acceleration

Complete separation in a reasonable period of time can only be achieved by mechanically generated centrifugal force. Fuel from the settling tank is fed to a centrifugal system or purifier and water and solids are separated out of the fuel. The rate of separation in a centrifugal field (V) is defined as:

$$V = V_g \times Z$$

Where Z equals $r \omega^2/g$ (r = distance of the particle from the axis of rotation, ω is the angular velocity). The factor Z specifies how much greater the sedimentation rate is in the centrifugal field compared to the gravitational field.

4a. Conventional cleaning with purifiers/clarifiers

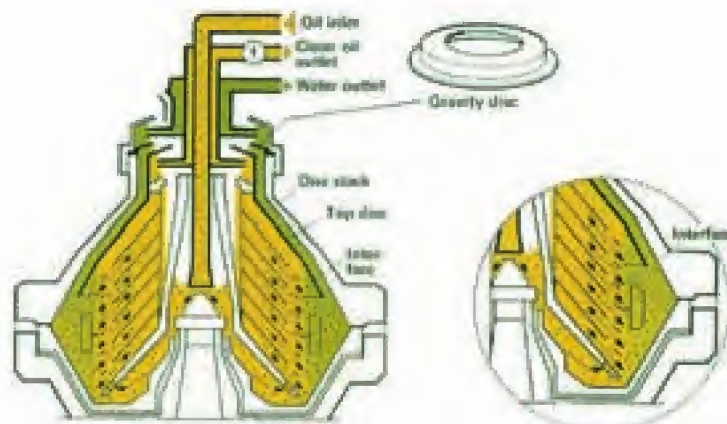
The increasing difference in density between water and fuel oil with increasing temperature is the base for centrifugal cleaning (purification).

In a purifier separator, cleaned oil and separated water are continuously discharged during operation. An interface is formed in the bowl between the water and the oil (see Figure 1). This interface position is affected by several factors, such as density and viscosity of the fuel oil, temperature and flow rate. Figure 2 illustrates that the position of the interface becomes progressively more sensitive with increasing fuel density. The generally accepted maximum density limit for a conventional purifier is 991 kg/m³ (at 15°C).

In order to achieve optimum separation results with purifiers, the interface between oil and water in the bowl must be outside the disc stack but at the inside of the outer edge of the top disc (detailed view in Figure 1). The position of the interface is affected mainly by the density and the viscosity of the fuel oil and is adjusted by means of gravity discs. The correct gravity disc is defined as the largest disc that does not cause a broken water seal. With the correct interface position, the oil feed can enter the narrow channels of the disc stack along its entire height. This is important since separation takes place in these channels.

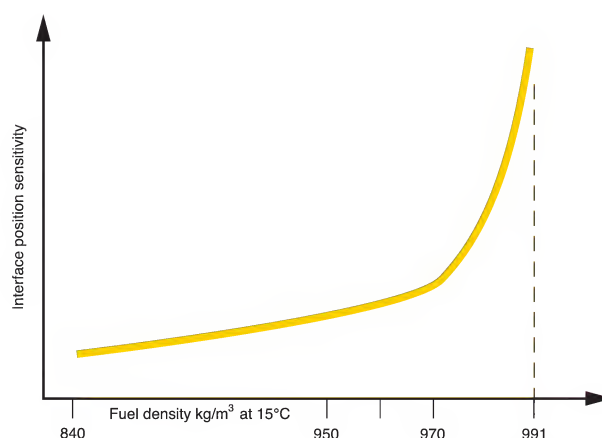
For fuel oils with a viscosity above 180 mm²/s at 50°C, it is recommended that the highest possible temperature (98°C) be maintained. The fuel oil has to remain in the centrifuge bowl for as long as possible by adjusting the flow rates through the centrifuge so that it corresponds to the amount of fuel required by the engine.

If the interface is in an incorrect position (see Figure 3), the oil to be cleaned will pass through only the lower part of the disc stack, since the upper part is blocked with water. Thus, separation is inefficient because only part of the disc stack is being used.



(Source: Alfa Laval)

Figure 1: Correct interface position – Oil distributed to all channels in the disc stack



(Source: Alfa Laval)

Figure 2: Interface position sensitivity

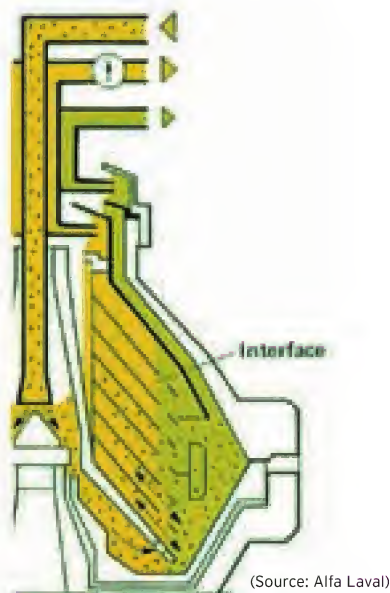


Figure 3: Incorrect interface position

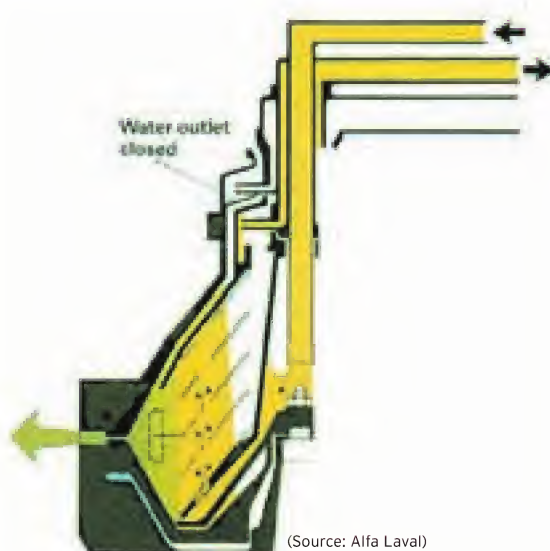


Figure 4: Conventional clarifier

To ensure optimal cleaning of a fuel oil, a second separator can be used in series operation, for example, a purifier followed by a clarifier. The density limit of 991 kg/m^3 is not applicable to clarifier operation, but the combined system of purifier and clarifier in series remains restricted to a maximum density of 991 kg/m^3 at 15°C . Heavy movements of the vessel can stir up dirt, water and sludge that have accumulated over time on the bottom of the bunker and settling tanks. Efficient purification is not always possible when separators have been put in a parallel purifying function.

In a conventional clarifier (see Figure 4), the water outlet is closed off and the separated water can only be discharged with the sludge through the sludge ports at the bowl periphery. A sludge discharge causes turbulence in the bowl and leads to less efficient separation. Consequently, the water handling capability of a conventional clarifier is insufficient for the cleaning of fuel oil if the fuel oil has a significant amount of water. (The prior use of a purifier with its continuous water removal is mandatory.)

4b. Advanced computer driven fuel cleaning systems

Example: ALCAP

Fuel oils with densities above 991 kg/m^3 at 15°C are available on the market and can be purified, for example, with the ALCAP system, which allows fuel oil densities up to 1010 kg/m^3 at 15°C . Fuel oil is continuously fed to the separator. The oil flow is not interrupted when sludge is discharged.

The ALCAP basically operates as a clarifier. Clean oil is continuously discharged from the clean oil outlet. Separated sludge and water accumulate at the periphery of the bowl. Sludge (and water) is discharged after a pre-set time. If separated water approaches the disc stack (before the pre-set time interval between two sludge discharges is reached), some droplets of water start to escape with the cleaned oil. A water transducer, installed in the clean oil outlet, immediately senses the small increase of the water content in the clean oil. A signal from the water transducer is transmitted to a control unit and changes in water content are measured.



Increased water content in the cleaned oil is the sign of reduced separation efficiency for not only water, but for the removal of solid particles, as well. When the water content in the cleaned oil reaches the pre-set trigger point, the control unit will initiate an automatic discharge of the water that has accumulated in the bowl through the water drain valve.

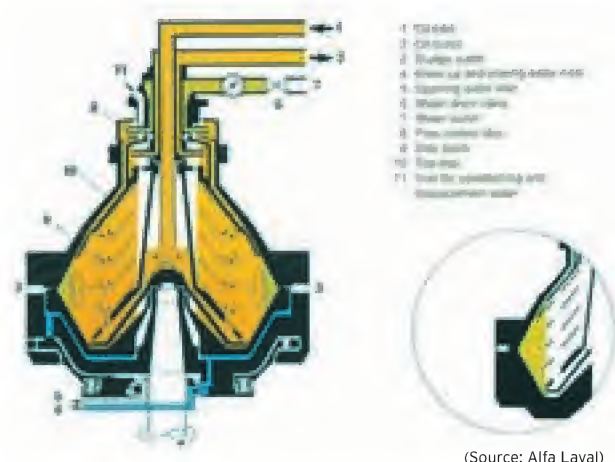


Figure 5: ALCAP separator

In summary, water is discharged either with the sludge at the periphery of the bowl (Figure 6a): separated water does not reach the disc stack in the pre-set time between sludge discharges, or through the water drain valve (Figure 6b): separated water reaches the disc stack before the pre-set time between sludge discharges.



Figure 6a: Discharge of separated water through sludge outlet

Figure 6b: Discharge of separated water through water drain valve

5. Fuel oil stability and compatibility

Total potential sediment is an important specification for heavy fuels. Currently, nearly all heavy fuel is marketed with the stability guarantee of total potential sediment (ISO 10307-2) 0.10 m/m % max. Stratification in heavy fuel oil tanks is minimal when this specification is met.

The reason for the specification requirement is the presence of asphaltenes in the heavy fuel. Asphaltenes are present in crude oil, and are defined as the fraction insoluble in n-heptane, but soluble in toluene. Their concentration in the crude oil is dependent on the crude oil origin itself. Asphaltenes are the highest molecular weight molecules in the crude, and contain all of the organically bound vanadium and most of the nickel found in the crude. They also contain a relatively high percentage of sulphur and nitrogen. Their hydrogen content (and hence, combustion characteristics) can be quite different from one crude to another. Asphaltenes have a predominantly aromatic structure and the C and H atoms are combined in ring structures as illustrated below.

Asphaltenes are polar molecules, kept in colloidal suspension² by their outer molecular structure. Thermally cracked asphaltene molecules have lost part of their outer structure (depending on the severity of the thermal cracking process), and even visbreaking, which is a relatively soft thermal cracking process, affects this outer molecular structure. If too much is removed, part of the asphaltenes can start clogging together, and will no longer be kept in suspension in the fuel matrix, sludge will be formed. Avoiding the formation of this sludge during the manufacturing of visbroken fuel is the responsibility of the refinery. A change in the fuel matrix composition by blending a stable visbroken fuel to a lower viscosity can also affect the stability of the asphaltenes. This means that viscosity reduction of a visbroken fuel with a paraffinic-type cutterstock can make the fuel unstable. When this happens, the two fuels are said to be incompatible. When two fuels that are mixed together do not cause any asphaltene coagulation, they are compatible with each other. Test methods exist to predict the final stability of a fuel mixture, and hence, the compatibility of the two components. In practice, one chooses a cutterstock with a high enough aromaticity to

² Colloidal suspension: a suspension in which gravitational forces are negligible

keep the asphaltenes dispersed (for example, by adding heavy and/or light cycle oil) and to provide an adequate stability reserve.

Two heavy fuels with diverse compositions (for example, one an atmospheric heavy fuel from paraffinic crude, and the other from a relatively severe visbreaker operation) can also be incompatible with each other. When storing fuel, the potential of compatibility problems between two different heavy fuels should be kept in mind.

6. Commingling of fuels

Indiscriminate commingling of fuels can lead to stability problems of the final fuel due to incompatibility of the fuels used as blend components. Eventual problems/damages arising from the commingling of fuels are the responsibility of the individual who made the decision to commingle the fuels. Fuel suppliers guarantee the stability of the fuel they deliver, but can not be held responsible for compatibility problems with another fuel.

Rules, in descending order of safety:

- Do not commingle fuels.
- If commingling is unavoidable, check the compatibility of the fuels in advance, and make a final decision based on the test result.
- If a compatibility check is not possible (one component unavailable at the moment the decision has to be made), reduce the amount of one fuel to a minimum before adding the second fuel.

Note: Generally fuels of the same viscosity grade with similar densities will be compatible.

7. Microbiological contamination

Plugging of filters on gasoil and marine distillate fuel feed lines can be caused by microbiological contamination (bacteria, fungi and yeast).

Microbiological contamination can always occur, especially if temperature conditions are favorable (between 15 and 40°C, for the most common types), and if non-dissolved water is present in the fuel.

NO WATER = NO MICROBIOLOGICAL CONTAMINATION

Microbiological contamination ideally occurs in tropical and sub-tropical regions: high air humidity combined with a high ambient temperature.

To avoid contamination, VOS, the Dutch organization that supervises the quality of gasoil delivered in the Netherlands, offers these points:

- Good water-housekeeping is essential.
- No water = no bacterial contamination
- Fuel-producing companies, dealers, and end-users have a common responsibility: Bacterial contamination can occur in each link of the chain.
- Consequences of bacterial contamination: filthy fuel system, plugged fuel filters and erratic engine operation
- Bacterial contamination can be found in slime, sludge, and as possible corrosion in filters, tanks, lines
- What the end-user can do:
 - Make sure no water enters the gasoil
 - Check filters
 - Check bunker and day tank for water
 - Whenever necessary, drain tanks. Secure permanent connection devices at the fuel receiving site
 - Have de-aerating openings which can be closed (to prevent waves entering the bunkertank)

On-site macroscopic (visual) examination offers a first screening between the contaminated and non-contaminated tanks. Possible microbiological contamination indicators are:

- Gasoil is hazy and/or contains suspended fluffy material
- Emulsion or a slimy interface layer between water and gasoil
- A turbid, badly smelling water bottom, with sludge-like deposits

Bacteria and fungi are the most important agents of microbiological contamination (yeast normally only occur as co-contaminant). All are living cells, which multiply through cell division.



The prime contamination of fuel is almost always by aerobic bacteria and/or by fungi. Both use the n.- paraffin fraction of the fuel as nutrient. Aerobic bacteria need oxygen for their metabolism and evolve at the interface between the water and the gasoil; fungi (aerobic) also attach themselves to the tank wall. When oxygen is no longer present, anaerobic bacteria start to develop. The anaerobic metabolism process generates hydrogen sulphide. Besides being a very dangerous toxin, hydrogen sulphide can also cause severe corrosion.

Anaerobic microbiological contamination should be avoided at all costs. Keep close control on the presence of microbiological contaminants in the complete fuel system, from manufacturing to end use. In regions with moderate climatic conditions, efficient water draining is often sufficient to avoid exponential growth; in sub-tropical and tropical climates, the continuous use of a biocide is often the only way to avoid problems. Biocides are also used worldwide to combat "imported" microbiological problems. Commercially available biocides have been developed to eliminate the total microbiological contamination (bacteria, fungi and yeast). There are two different types of biocides: water soluble and oil soluble. To eliminate microbiological contamination in fuel tanks, water soluble biocides are generally the most cost-effective. The treat rate can differ according to the type and severity of the contamination (and the amount of non-removable water). Water drained from tanks after a biocide treatment cannot be sent directly to a biological water purification system; the biocide has to be deactivated first.

8. Fuel contamination in lubricants

In the 1990s, the demands on marine lubricants changed considerably for medium-speed engines. Operating the engines at higher thermal and mechanical loads made it more difficult for the lubricant to cope with the issues of borderline lubrication. At the same time, engine design changes, such as the introduction of the anti-bore polishing ring, decreased oil consumption in medium-speed engines considerably from 1-1.5 g/kWh or more to 0.4-0.7 g/kWh or lower in modern engines.

Changes to engine construction and the deterioration of heavy fuel quality, which began in the late 1970s, spawned significant challenges to marine lubricants. Liner lacquering, undercrown deposits, increased oil consumption, base number depletion, hot corrosion of the piston crown, oil scraper ring clogging and increased piston deposits occurred. As a result, formulations needed to be adapted.

Medium-speed engine blackening due to HFO contamination of the lubricant, piston head corrosion and undercrown deposits were typical consequences of increased fuel pump pressure and the switch-over from atmospheric heavy fuel to visbroken heavy fuel.

It's possible for HFO to enter the lubricant directly as a result of leaking fuel pumps, or unburned HFO that remains on the cylinder walls can be washed down into the sump. HFO contamination can now be assessed by measuring the concentration of unburned asphaltenes in the lubricant. Chevron Global Marine Products, in cooperation with MAN Diesel in Augsburg, developed a test method which accurately measures this concentration (in %wt) and also qualifies the origin of the asphaltene ingress. The typical contamination level of medium-speed engine oil with asphaltenes, as measured by Chevron Technology Ghent during the last ten years, has been between 0.25 and 0.30%wt.

Common issues encountered with conventional lubricant due to HFO contamination:

1. Engine blackening

The increase of the fuel pump pressure up to 1600 bar in medium-speed diesel engines results in a higher fuel pump leakage, meaning increased fuel contamination. Most HFOs originate from visbreaking installations. The asphaltenes don't dissolve in the paraffinic lubricant, instead they coagulate and form floating asphalt particles of 2 to 5 microns in the lubricant. These particles are very sticky and form black deposits on all metal surfaces of the engine. This then results in black deposits in the cambox and in the crankcase. These deposits cause oil scraper ring clogging, sometimes resulting in high oil consumption. They may form deposits in the hot areas of the piston grooves and on the piston lands and in the cooling spaces of the piston.

If an oil barrier is used to seal the fuel pump, asphaltene coagulation can occur on the surface of the fuel pump plunger, at times resulting in fuel pump blockages. These deposits can obstruct the fuel pump drain. This results in excessive fuel ingress into the lubricant, aggravating the deposit problems and causing serious viscosity increases due to fuel admixture. These problems can be minimized by effectively removing the asphalt particles from the lubricant.

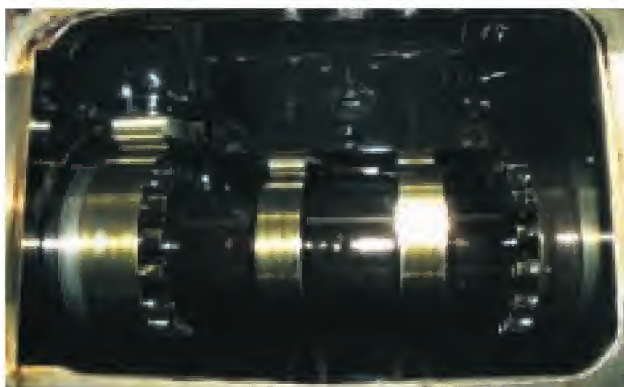


Figure 7: Conventional lubricant



Figure 8: Conventional lubricant – showing heavy fuel contamination

2. Undercrown deposits and piston head corrosion

The tendency to increase the piston undercrown temperature can result in carbon deposits on the piston undercrown due to thermal carbonization of the lubricant. Also, asphalt particles originating from HFO can adhere to the piston undercrown when conventional lubricants are used.

Undercrown deposits combined with high load operations can lead to piston head corrosion. Undercrown deposits cause a reduction in the cooling effect, resulting in about 100°C increase in piston temperatures. Above 450°C, some Na/V oxides (when present) can melt with the piston crown material causing hot corrosion on the top of the piston.

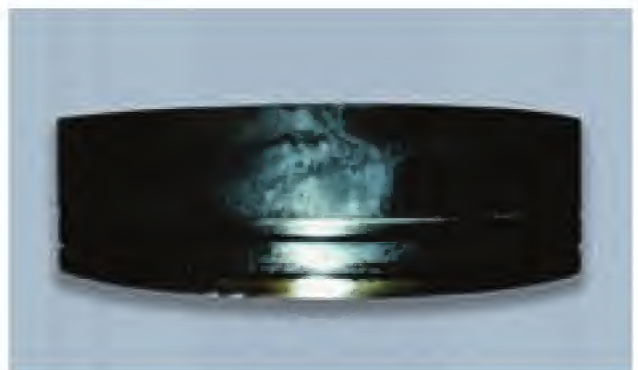


Figure 9: Conventional lubricant – typical piston deposits in a medium-speed engine with heavy fuel contamination



Figure 10: Conventional lubricant – typical oil scraper deposits in a medium-speed engine with heavy fuel contamination

To respond to the HFO challenges, Chevron Global Marine Products developed a lubricant series with high asphaltene dispersancy, to optimize lubrication of medium-speed engines and to avoid the issues resulting from asphaltene contamination. TARO DP/XL (available as a 20, 30, 40, 50 or 60 BN) were developed specifically to cope with increasing mechanical and thermal stresses and the changes in fuel quality. Since its introduction in the mid-1990s, the Taro DP/XL series has demonstrated excellent performance in a wide range of medium-speed engine types. Taro DP/XL is currently recognized as a top-tier product technology for medium-speed engine lubrication.

Figure 11 illustrates the cambox cleanliness obtained with TARO DP technology, compared with the blackening of the cambox using a conventional lubricant, as illustrated in Figure 8.



Figure 11: Taro DP technology – cambox cleanliness despite 4% heavy fuel contamination

Attachments



Attachment I: Crude oil refining

The purpose of crude oil refining is to convert crude and other feedstocks into saleable products. The desired products are mainly gasoline, kerosene, jet fuel, gasoil and diesel.

In order to obtain these products, crude oil is first separated into fractions by distillation, then the different fractions are further processed in order to obtain the desired characteristics and optimum yield.

The different processes used in a modern refinery are:

1. Crude oil desalting

Water and inorganic salts are removed in an electrostatic field. The main purpose of crude oil desalting is to protect the refining process units against corrosion.

2. Atmospheric distillation

Crude oil is a product with a very wide boiling range. In an atmospheric distillation column the fractions boiling below 360°C are distilled off under reflux, and, according to boiling range, recovered as naphtha, kero, and gasoil type stocks. Atmospheric distillation is limited to a maximum temperature of 360°C, because otherwise coking would start to occur, which is not desirable at this stage of crude oil refining.

3. Vacuum distillation

In order to distill off a heavier cut without exceeding the 360°C temperature limit, a second distillation is done under reduced pressure: the vacuum distillation. The distillate fraction of the vacuum distillation unit is the feedstock for a catalytic cracking unit (see item 4).

4. Catalytic cracking (for example, fluidized bed catalytic cracking)

The main feedstock for a catalytic cracker is vacuum gasoil. The cracking operation breaks large molecules into smaller, lighter molecules. The process runs at high temperatures, and in the presence of the appropriate catalyst (crystalline aluminum silicate).

Atmospheric residue, with a low metal and MCR content, can also be used as catalytic cracker feed, necessitating an adjustment of the catalyst type.

The main purpose of a catalytic cracker is to produce light hydrocarbon fractions, which will increase the refinery gasoline yield.

Additional streams coming from the catalytic cracker are light cycle oil (increases the gasoil pool) and heavy cycle oil (base stock for carbon black manufacturing). Both streams are also used in heavy fuel oil blending.

5. Catalytic hydrocracking

Some refineries use catalytic hydrocracking as a supplementary operation to catalytic cracking. Catalytic hydrocracking further upgrades heavy aromatic stocks to gasoline, jet fuel and gasoil material. The heaviest aromatic fractions of a cat cracker are the normal feedstock for a hydrocracker. Hydrocracking requires a very high investment, but makes the refinery yield pattern nearly independent from the crude oil feed.

6. Visbreaking

The feedstock of a visbreaker is the bottom product of the vacuum unit, which has an extremely high viscosity. In order to reduce that viscosity and to produce a marketable product, a relatively mild thermal cracking operation is performed. The amount of cracking is limited by the overruling requirement to safeguard the heavy fuel stability. The light product yield of the visbreaker (around 20%) increases the blendstock pool for gasoil.

7. Coking (delayed coking, fluid coking, flexicoking)

Coking is a very severe thermal cracking process, and completely destroys the residual fuel fraction. The yield of a coker unit is lighter-range boiling material, which ultimately goes to the blending pool for the lighter products, and coke, which is essentially solid carbon with varying amounts of impurities. The heavier distillate fraction of a coker can be used as feedstock for a hydrocracker (see item 5).

More processes are required before the end products leave a refinery. Most processes are designed to meet the technical requirements of the end products, others are needed to meet environmental limits (mainly sulphur reduction, both in the end products and in the refinery emissions).

8. Catalytic reforming and isomerization

Both processes are catalytic reforming, and are intended to upgrade low-octane naphtha fractions of the crude distillation unit into high octane components for gasoline production. The type of catalyst and the operating conditions determine if the reforming is mainly to



iso-paraffins or to aromatics. The terminology “reforming” is generally used for the change to aromatics, while the change to iso-paraffins is referred to as “isomerization”. Isomerization is normally done on a lighter fraction (C5/C6), while reforming is done on the heavy naphtha fraction (C7 and heavier, up to 150°C).

9. Alkylation

This is another process intended to increase the yield of valuable gasoline blend components. Alkylation is a catalyst-steered combination reaction of low molecular weight olefins with an iso-paraffin to form higher molecular weight iso-paraffins. The feed to the alkylation unit is C3 and C4s from the catalytic cracker unit and iso-butane.

10. Hydrotreating

Hydrotreating process is a process that uses hydrogen to remove impurities from product streams, while replacing these impurities by hydrogen. When hydrotreating is used to remove sulphur (very low sulphur limits in the specifications of gasoline and gasoil), it is called hydro-desulphurization. It is a catalytic process. The process is generally used on kerosene and gasoil fractions. Residual hydro-desulphurization is also a process, and is feasible, but not economical.

11. Merox

A merox unit is used on naphtha and kerosene streams. It is a catalytic process which is not intended to remove the sulphur from the stream, but to convert mercaptan sulphur molecules (corrosive, and obnoxious smelling) into disulphide type molecules.

12. Sulphur recovery

As a result of the removal of sulphur from the refinery streams by hydrotreating, and the generation of hydrogen sulphide during cracking and coking, refinery gases contain a very high concentration of hydrogen sulphide. The simple solution to eliminate the highly toxic hydrogen sulphide is to burn it, but this then generates SO_2 , which contributes to acidification problems. In order to safeguard the environment, the hydrogen sulphide is converted in refineries to elemental sulphur. This is typically accomplished by extracting the hydrogen sulphide from the refinery gas by a chemical solvent, for example, an aqueous amine solution. The rich solution is then preheated and stripped by steam.

The Claus process consists of the partial combustion of the hydrogen sulphide rich gas stream (sufficient air is introduced to combust 1/3 of the H_2S to SO_2). This SO_2 then reacts (under influence of a catalyst) with H_2S in the order of one SO_2 for two H_2S , and thus provides elemental sulphur. The tail gas of the Claus unit is still rich in SO_2 , and environmental legislation can require the further clean-up of this tail gas.

Attachment II: Reproducibility (R) of marine fuel test methods

Density at 15°C, kg/m^3

1. ISO 3675

For transparent, non viscous products:

$R = 1.2 \text{ kg/m}^3$ or 0.0012 kg/l

For opaque products: $R = 1.5 \text{ kg/m}^3$ or 0.0015 kg/l

2. ISO 12185

For transparent middle distillates:

$R = 0.5 \text{ kg/m}^3$ or 0.0005 kg/l

For crude oils and other petroleum products:

$R = 1.5 \text{ kg/m}^3$ or 0.0015 kg/l

Kinematic viscosity, mm^2/s

ISO 3104

Heavy fuels: at 50°C : $R = 0.074x$

Where x is the average of the results being compared

Flash point, P.M., closed tester

ISO 2719

Procedure A (distillate fuels) : $0.071x$

Where x is the average of the results (°C) being compared

Procedure B (residual fuel oils) : 6°C

Pour Point, °C

ISO 3016

$R = 6.59^\circ\text{C}$

Cloud Point, °C

ISO 3015

For distillate fractions: $R = 4^\circ\text{C}$

Sulphur, % (m/m)

1. ISO 8754

$$R = 0.00812(x + 0.15)$$

Where x is the mean sulphur content

2. ISO 14596

For sulphur content in the range 0.10-0.99 m/m

$$\% : R = 0.02$$

For sulphur content in the range 1.00-2.50 m/m

$$\% : R = 0.04$$

Cetane index (4 variable equation)

ISO 4264

Precision depends on the precision of the original density and distillation recovery temperature calculations.

Micro carbon residue, % (m/m)

ISO 10370

$$R = X^{2/3} \times 0.2451$$

Where X is the average of the results being compared

Ash, % (m/m)

ISO 6245

For ash content between 0.001 and 0.079 wt %:

$$R = 0.005$$

For ash content between 0.080 and 0.180 wt %:

$$R = 0.024$$

Total existent sediment, % (m/m)

ISO 10307-1

Heavy fuels: $R = 0.294 \sqrt{x}$

Distillate fuels containing heavy components:

$$R = 0.174 \sqrt{x}$$

Where x is the average of the test results in % (m/m)

Total potential sediment, ageing, % (m/m)

ISO 10307-2

Heavy fuels: $R = 0.294 \sqrt{x}$

Distillate fuels containing heavy components:

$$R = 0.174 \sqrt{x}$$

Where x is the average of the test results in % (m/m)

Water, % (v/v)

ISO 3733

Water collected between 0.0 and 1.0 ml:

$$R = 0.2 \text{ ml}$$

Water collected between 1.1 and 25 ml: $R = 0.2 \text{ ml}$ or 10% of mean, whichever is greater

Vanadium, mg/kg

1. ISO 14597

The method is applicable to products having V content in the range of 5 to 1000 mg/kg, although reproducibility data have only been determined up to 100 mg/kg for V

For V content between 5-30 mg/kg: $R = 5 \text{ mg/kg}$

For V content between 31-100 mg/kg:

$$R = 10 \text{ mg/kg}$$

2. IP 501

$$R = 1.6799 x^{0.6}$$

Where x is the average of the results (mg/kg) being compared

3. IP 470

$$R = 3.26 x^{0.5}$$

Where x is the average of the results (mg/kg) being compared

Cat fines Al+Si, mg/kg

1. ISO 10478, IP 501

ICP detection:

$$\text{Al: } R = 0.337x$$

$$\text{Si: } R = 0.332x$$

Where x is the average of the results (mg/kg) being compared

2. IP 470

AAS detection:

$$\text{Al: } R = 0.789 x^{0.67}$$

$$\text{Si: } R = 1.388 x^{0.67}$$

Where x is the average of the results (mg/kg) being compared

Ca, Zn, P, mg/kg

1. Ca

$$\text{IP 501 (ICP) } R = 0.6440 x^{0.65}$$

$$\text{IP 470 (AAS) } R = 1.139 x^{0.8}$$

2. Zn

$$\text{IP 501 (ICP) } R = 0.5082 x^{0.7}$$

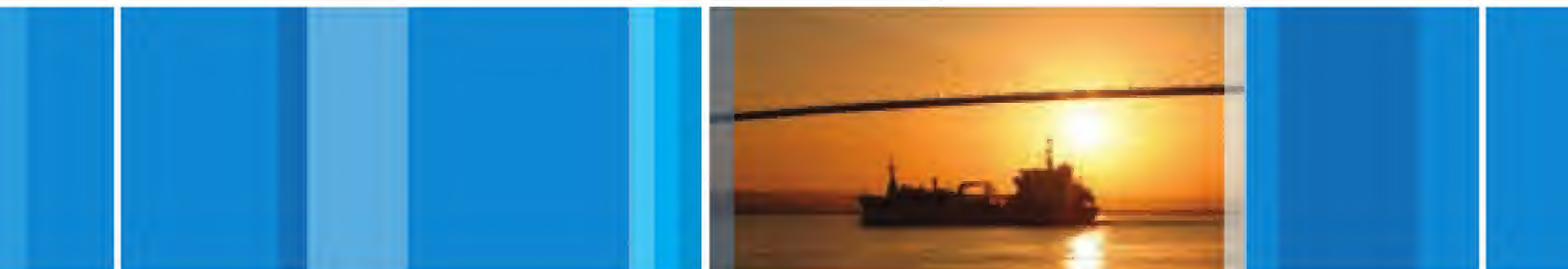
$$\text{IP 470 (AAS) } R = 0.580 x^{0.75}$$

3. P

$$\text{IP 501 (ICP) } R = 1.2765 x^{0.55}$$

$$\text{IP 500 (UV) } R = 1.2103 x^{0.4}$$

Where x is the average of the results (mg/kg) being compared



Attachment III: Gas turbine fuel requirements

Most heavy-duty gas turbines operate on natural gas and distillate fuels. Gas turbines operating on natural gas require minimum fuel treatment. Distillate fuels, immediately after refining, have no or extremely low contamination levels of water, solids and trace metals. Contamination (mainly by water) during transport can not be excluded, and centrifuging is the best method for the removal of water and solids. Sodium salts are very detrimental for gas turbines, and seawater contamination must be completely removed.

Gas turbine manufacturers have also developed efficient technologies for gas turbine operation with ash forming fuels (for example, heavy fuels), as a cost-effective option instead of gasoil for sites where natural gas will not be available in the foreseeable future.

The use of heavy fuels requires that attention be paid to two types of potential hot path corrosion:

- Sulphidation corrosion, caused by alkaline sulphates (mainly Na_2SO_4)
- Vanadic corrosion, caused by low melting vanadium oxides (V_2O_5)

Sulphidation corrosion is avoided by removing the sodium and potassium from the fuel by stringent water washing up to the level $\text{Na} + \text{K} < 1 \text{ mg/kg}$. Vanadic corrosion is counteracted by the addition of magnesium additives to the fuel from the moment $\text{V} > 0.5 \text{ mg/kg}$. The complex oxides between Mg and V which are then formed, are no longer corrosive (traditionally, a m/m ratio Mg/V of three is adhered to).

Heavy-duty gas turbines have been operating satisfactorily on ash forming fuels since the mid-1980s. It is clear that the need to use magnesium-based additives to combat vanadic corrosion imposes a technical and economical upper limit on the vanadium content of the fuel.



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VOS, Publication Stichting VOS

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